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The preparation, properties, and industrial possibilities of the allyl ether of starch were described in 1945 (2). Since that time great interest has been shown in this polyallyl derivative, principally because of its solubility in organic solvents, the ease with which its films become hard and insoluble on exposure to air, and the low cost of the raw materials--starch and allyl chloride--used in its manufacture. In spite of the attractive features of allyl starch and the promising results obtained in evaluation studies in several industrial laboratories, commercial production and utilization have been handicapped by lack of an efficient method for preparing it.

The greatest objection to the previously described method is the fact that a large excess of allyl chloride is required (600% more than that theoretically needed to substitute two allyl groups per glucose unit), and although part of the allyl chloride and its reaction byproducts could be recovered, the process still does not appear economical enough for production of allyl starch on a large scale. Because of the need for a more efficient method, we have studied the allylation of starch and some of the variables involved. This paper reports satisfactory methods requiring only 35 to 50% excess allyl chloride. Although these methods are not considered final, they are reported because it is believed that the information will be useful to investigators in various industrial organizations currently working on allyl starch.

### Laboratory Method for the Preparation of Allyl Starch

**APPARATUS:** A 5-liter, three-neck, round-bottom flask was fitted with a loop-type stirrer and a Friedrichs condenser without a drip tip. The third neck was closed with a glass stopper. Our stirrer was made from Monel rods (main shaft, 3/8", stirring loops, 1/8"). The flask was mounted in a bath which could be controlled at 80° C. The mounting must be strong, since during the reaction the mixture in the flask becomes semisolid. The stirrer was driven through a "V" belt at approximately 200 r.p.m. (a) by a 1/8 horse-power motor.

**PROCEDURE:** The bath was filled with water at room temperature, and the bath stirrer started. Air-dry starch<sup>(b)</sup> (750 g.) was pasted in the flask with 700 g. of 50% sodium hydroxide at a temperature below 30° C. The starch and alkali were mixed to a smooth paste<sup>(c)</sup>. Then 1500 cc.

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of methylethyl ketone was stirred in, followed by 795 cc. of allyl bromide<sup>(d,e)</sup> (35% more than the theoretical for two allyl groups). At this stage the starch and alkali layer looked like a smooth white paste below the organic layer. The bath heaters were now turned on, and the bath was heated to 80° in approximately 25 minutes. When the bath temperature reached 50-60° C., the two layers began to mix, and soon the starch was dispersed throughout the mixture as sandy looking material. Soon after the bath reached 80° C. the reaction mixture began to boil rapidly, and the condensate ran from the condenser in a steady stream. The rate of boiling slowed down as the reaction proceeded. In about an hour after reaching 80°, the reaction mixture became noticeably more viscous, and in two to three hours it became semisolid. The heating and stirring were continued until the reaction mixture became neutral (pH, 6-8, Hydrion pH paper), which required 8-10 hours<sup>(f)</sup>. Sufficient concentrated hydrochloric acid (20-25 cc.) in methylethyl ketone (100 cc.) was introduced into the reaction mixture at this point to bring the acidity to pH 2-3. The mixture gradually became less viscous and acquired an orange color. Heating and stirring were continued for another hour or two, or until the allyl ether became soluble in the reaction mixture. At this point, sodium bromide rapidly settled when the stirrer was stopped. At the end of the reaction, the hot water in the bath was replaced with cold water. After awhile the solution of allyl starch was decanted, and the salt cake on the bottom of the flask rinsed with a little solvent. To the combined solutions of allyl starch a little water was added, and the solution was rapidly steam distilled until the vapor temperature reached 90-95° C., which required 30-50 minutes. At this stage the allyl starch was a canary-yellow doughy mass. It was then kneaded with warm (40-60° C.) running water until the salt was removed. The gummy material could be purified by dissolving it in acetone and precipitating the filtered solution with several volumes of water.

**COMMENTS:** (a) Actual rate of stirring in our apparatus. The rate of stirring and the efficiency of the stirrer affect the time of the reaction. (b) Potato starch was used in most experiments. Corn starch gives the same results. (c) It does not seem to make any difference in which order starch and alkali are added. The alkali solution can be prepared in the reaction flask but must be cooled to below 30° C. before the starch is added. A slight increase in the amount of alkali added (375-385 g. sodium hydroxide instead of 350 g.) seems to improve the substitution somewhat but requires more acid later. There seemed to be a slight improvement in the substitution when half the alkali was added as 50% solution and the other half as solid flakes. (d) Addition of allyl bromide portionwise might have a slight advantage. (e) Replacing methylethyl ketone with toluene has the advantage in easier separation of allyl starch solution from the rest of the reaction mixture but requires more efficient stirring during the reaction. (f) The reaction can be run continuously or interrupted for the night.

**RESULTS:** The results of 25 runs by this method and modifications of it can be summarized by stating that the average yield was 717 g., or 76% of the theoretical. The average substitution was 1.8 allyl groups per glucose unit.

## Preparation of Allyl Starch by the Use of Allyl Chloride

These preparations were carried out in a Pfaudler two-gallon glass-lined laboratory kettle with a closed anchor-type stirrer. The stirrer was driven through a reducer by a 1/3 horse-power motor at a rate of 55-60 r.p.m. The jacket of the reaction vessel was piped so that either steam, cold water, or hot water from a controlled bath could be circulated through it.

The general method was as follows: Air-dry potato starch (875 g., 13% moisture) was pasted with 980 g. of 50% sodium hydroxide solution. The alkali solution could be prepared in the reaction kettle and cooled to below 30° C. and then the starch could be mixed in, or the starch could be put in the kettle first and the cooled alkali solution then added. After the starch was thoroughly pasted, allyl chloride (985 g., 37% more than theoretical for two allyl groups) and acetone (3-5 liters) were added. The kettle was closed and heated to the operating temperature with steam (15-20 min.), and then hot water was circulated through the jacket to maintain the reaction mixture at about 90° C. The material showed signs of reaction when the temperature reached 50-60° and the lower starch layer began to mix with the upper organic layer. The pressure rose to about 40 pounds and then began to decrease gradually. After 3-5 hours the mixture became a thick, semisolid paste. After about 10 hours (continuous heating or allowing the kettle to cool to room temperature overnight), the kettle was cooled and opened. The pH (Hydrion paper) of the mixture ranged from 7 to 9 at this stage. Sufficient concentrated hydrochloric acid (30-40 cc.) mixed with acetone was added to bring the pH to 3 or slightly lower. Then the kettle was closed and heated to the reaction temperature and held there until the doughy material dissolved, which required about an hour. At this point the salt settled if the stirrer was stopped. After the material was in solution, the kettle was cooled by circulating cold water. The solution was then removed by siphoning it with suction into the 3-gallon Pyrex bottle used for steam distillation. The mixture was steam distilled and worked up in the same manner as the allyl bromide preparations. Approximately 80% of the acetone used could be recovered from the steam distillate.

Ten batches of allyl starch made by this method gave an average yield of 937 g., or 86% of theory, of gummy material (on dry basis). The average substitution was 1.65 allyl groups per glucose unit.

The addition of 1% of sodium iodide (based on the weight of starch) improved somewhat the substitution of the final product. For ten experiments the average yield was 957 g., or 87%, and the substitution, 1.8 allyl groups per glucose unit. Increasing the amount of alkali from 490 g. to 540 g. (with sodium iodide present) increased the substitution to 1.9 groups and the yield to 90% (990 g.) (average of five experiments). Larger amounts of acid were needed for solubilization of the product at the end of the reaction (about 100 cc.).

## Other Modifications of the Preparation of Allyl Starch

Two side reactions are known to take place during the preparation of allyl starch described above. Hydrolysis of allyl chloride in the presence of alkali has been discussed in a previous article (2) on the subject, and the situation has been taken care of, at least in part, by the use of concentrated alkali solution. The other side reaction is the one between the alkali and the acetone used as a solvent, which results in the formation of mesityl oxide and other condensation products of acetone. Although formation of the acetone condensation products does not affect adversely the preparation of allyl starch, it complicates the recovery of the solvent. Substitution of methylethyl ketone for acetone, a slightly more expensive but less reactive substance, reduces the amount of side products formed. However, complete elimination of ketones might be desirable. Toluene has several advantages over acetone. It is inexpensive, unreactive under the conditions of the experiment, immiscible with water (which facilitates separation of the final products), and readily recovered. On the other hand, the immiscibility of toluene with water retards the reaction somewhat, and requires better stirring facilities. When the batches were made with allyl bromide in a glass flask, in which good stirring was available, products of good substitution were obtained. In our autoclave the stirring was slower and less efficient, which slowed down the reaction considerably when toluene was used as a solvent. It required about 15 hours to bring the reaction mixture to pH 7, and it required several hours more to dissolve the product in solution after addition of acid. The substitution of allyl starch prepared in this manner was 1.5 allyl groups per glucose unit.

It seems that the presence of acetone or other solvent in the reaction mixture has a twofold function. Perhaps its most important role is to dissolve the allyl starch after the allylation has been completed. Besides, the presence of the solvent moderates the markedly exothermic reaction of etherification. A number of preparations have been made without solvents during the reaction in the following manner. In all these experiments, 50% excess allyl chloride was used instead of 37%.

A smooth paste was made with 800 g. of air-dry starch and 980 g. of 50% sodium hydroxide at room temperature. To this paste 1% of sodium iodide and 985 g. of allyl chloride were added, and the mixture was slowly heated in the closed autoclave. The reaction started before the mixture reached the usual temperature of reaction (90° C.). The pressure rose to about 60 pounds. On further heating at 90°, the pressure gradually dropped to 15-20 pounds, indicating that the reaction was over. This required about four hours. At this point acetone (3-5 liters) and hydrochloric acid (40-50 cc.) were introduced into the reaction mixture, and on further heating for about one-half hour the allyl starch was in solution. It was then steam distilled and purified as described above. An average yield of five preparations was 861 g., or 90% of theoretical, and the substitution of the product was 1.6 allyl groups per glucose unit. An attempt was made to reduce further the amount of water in the reaction mixture by adding half the amount

of alkali required as 50% solution and the other half as solid flakes. The average result of three experiments was: Yield, 813 g., or 84%, substitution, 1.65 groups. The decrease in yield and only slight increase in substitution were due to stirring difficulties of a mixture containing little liquid. The method was therefore further modified by adding part of the acetone (500 cc.) to the reaction mixture, which was then as follows: starch, 800 g.; 50% sodium hydroxide, 490 g.; solid sodium hydroxide, 245 g.; sodium iodide, 8 g.; acetone, 500 cc. The rest of the acetone was added with the acid after the etherification reaction was complete. The average for three preparations was: Yield, 927 g., or 92%; substitution, 1.8 allyl groups per glucose unit.

The analytical procedure for determination of unsaturation of allyl ethers of starch has been described in a previous article (1).

#### Literature Cited

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